Electronic Supplementary Information

Exploring and Exploiting the Synergy of Non-Covalent Interactions on the Surface of Gold Nanoparticles for Fluorescent Turn-On Sensing of Bacterial Lipopolysaccharide

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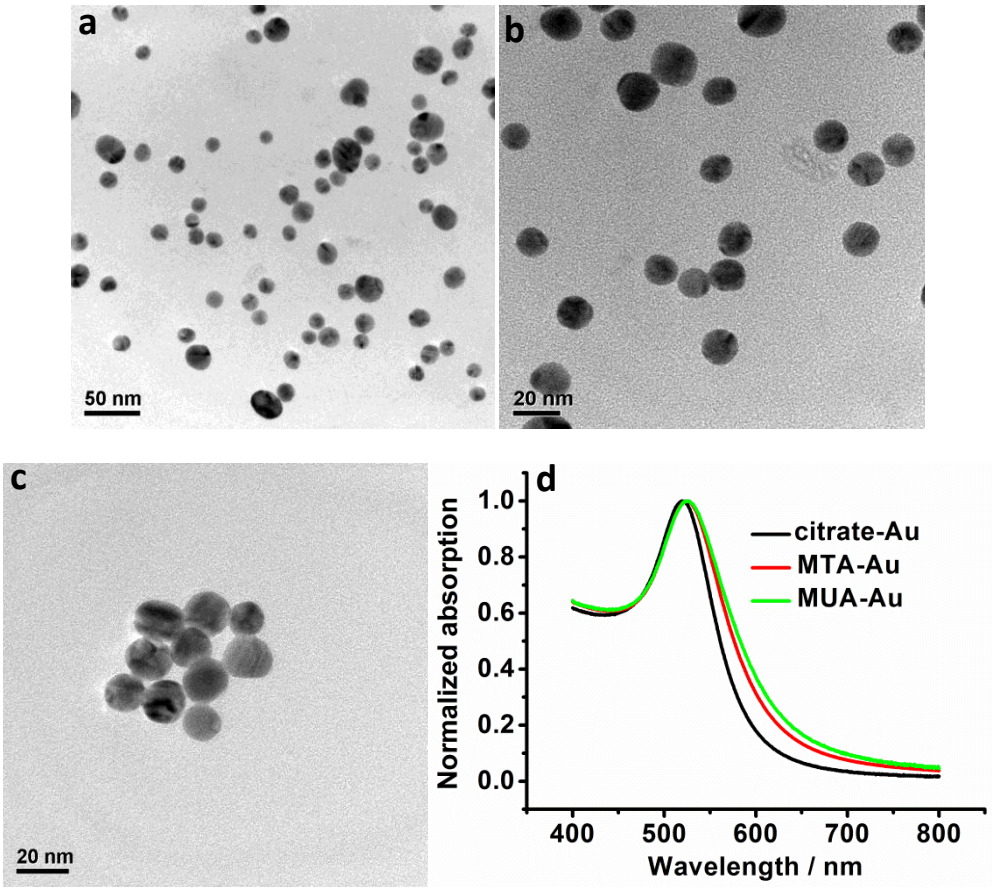

Figure S1. TEM images of sodium citrate coated Au NPs, citrate-Au (a), MTA-Au (b), and MUA-Au (c); UV-Vis absorption spectra of various Au NPs (d).

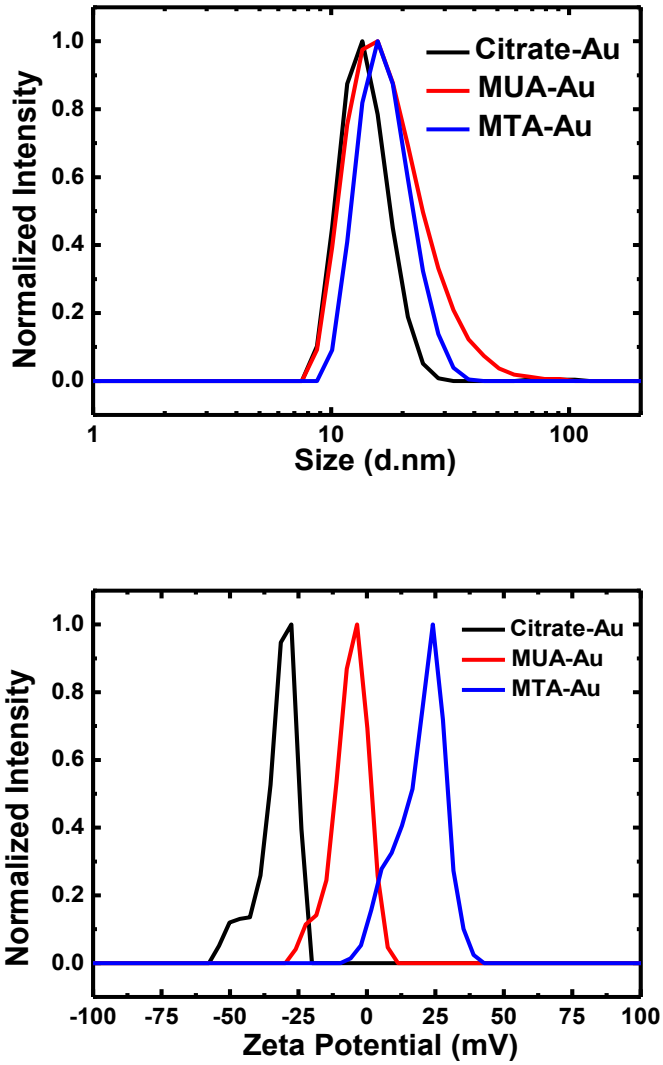

Figure S2. Hydrodynamic size of citrate-Au, MUA-Au and MTA-Au measured by DLS (top); Zeta-potential (bottom) of citrate-Au in water and that of MUA-Au and MTA-Au in 10 mM HEPES buffer (pH 7.0).

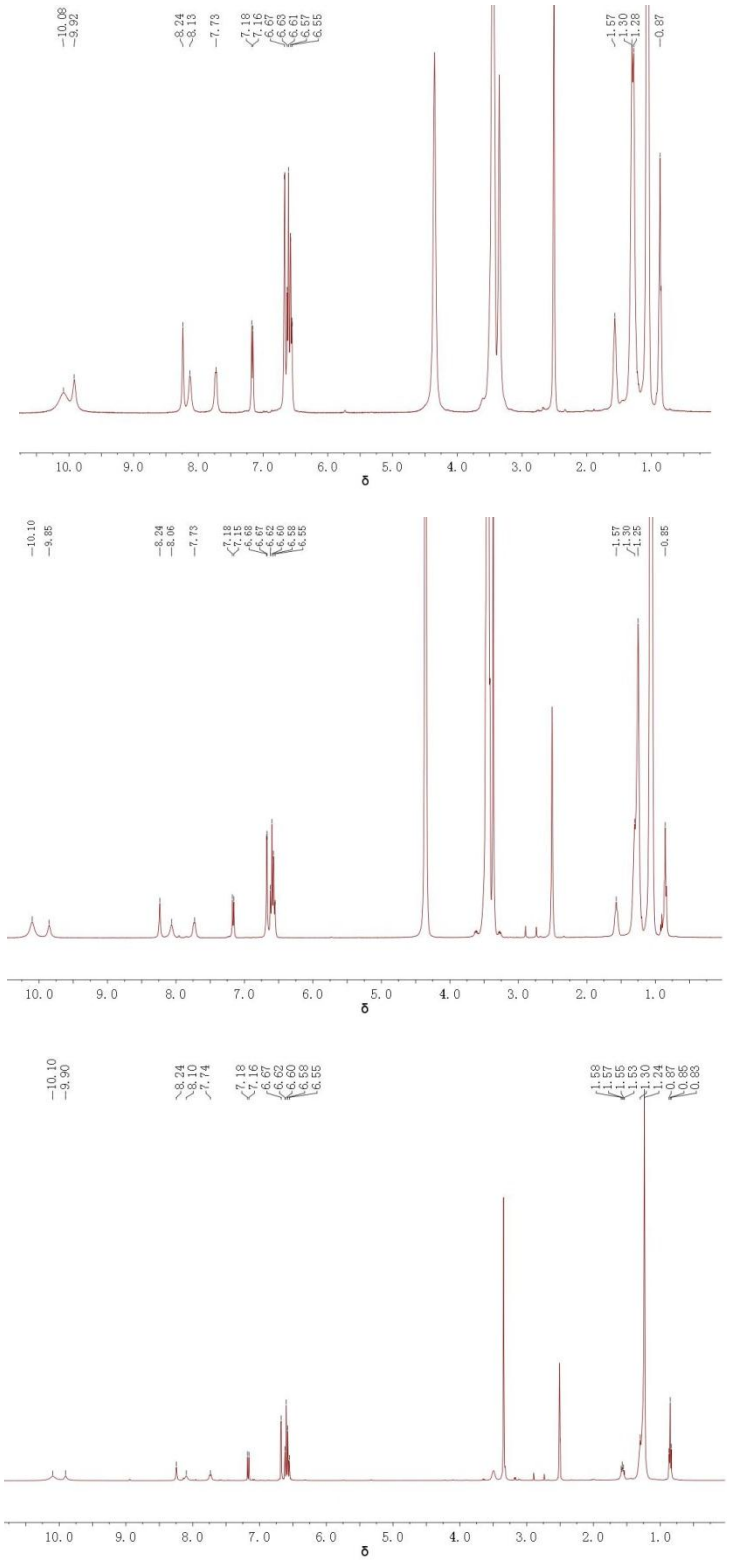

Figure S3. ^{1}H NMR Characterization of fluorescent probes (**2**-**4**); up: ^{1}H-NMR of **2**; middle: ^{1}H-NMR of **3**; bottom: ^{1}H-NMR of **4**. The peaks in 4.5 ppm, 3.5 ppm, and 1 ppm are from ethanol residual, and the peak in 3.4 ppm and 2.5 ppm is from DMSO and H_2O, respectively.

Hill equation

The quenching of fluorescence can be quantified by:

$$Q = \frac{F_0 - F}{F_0} \qquad (1)$$

where F_0 and F are fluorescence intensities of fluorescence probes **1**-**4** in the absence and presence of Au NPs, respectively.

The saturation value of Q can be defined as that Q_{max}:

$$Q_{\max} = \frac{F_0 - F_\infty}{F_0} \qquad (2)$$

where F_∞ is the fluorescence intensity of **1**-**4** on the surface of Au NPs. Considering the super-high quenching efficiency of Au NPs to fluorescent probes (i.e., the fluorescence of the probes can be completely quenched upon binding on the surface of Au NPs), the value of F_∞ is set to 0. Thus, the Q_{max} can be assigned to 1.

We assume that the binding of fluorescent probes (**1**-**4**) to Au NPs occurs at equilibrium, and the fluorescence quenching data can be fitted by Hill equation with the introduction of K_d and n which describes the binding constant of **1**-**4** to Au NPs and the Hill coefficient, respectively. The Hill equation can be described as the following:

$$\frac{Q}{Q_{\max}} = \frac{[\mathrm{Au}]^n}{(K_d^n + [\mathrm{Au}]^n)} \qquad (3)$$

where [Au] is the concentration of Au NPs.

By combining eq1, eq2, and eq3, the Hill equation can then be obtained as:

$$\ln\frac{F_0 - F}{F} = n \cdot \ln[\mathrm{Au}] - n \cdot \ln K_d \qquad (4)$$

This equation describes the quantitative relationship between fluorescence intensity of **1**-**4** and the concentration of Au NPs. By fitting the fluorescence quenching data with eq4, the binding constant K_d and Hill coefficient n of the binding of **1**-**4** to Au NPs can then be obtained.

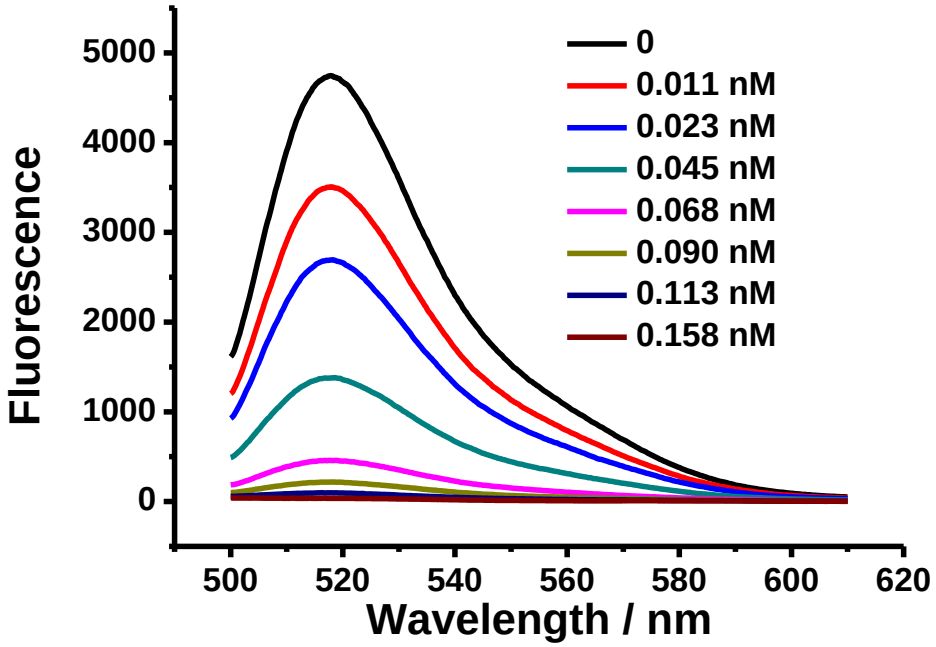

Figure S4. Fluorescence titration spectra of **3** in HEPES buffer solution upon the gradual addition of MTA-Au with the concentration ranging from 0 to 0.158 nM; the excitation wavelength is 490 nm. Fluorescence titration spectra of **2** and **4** were not given.

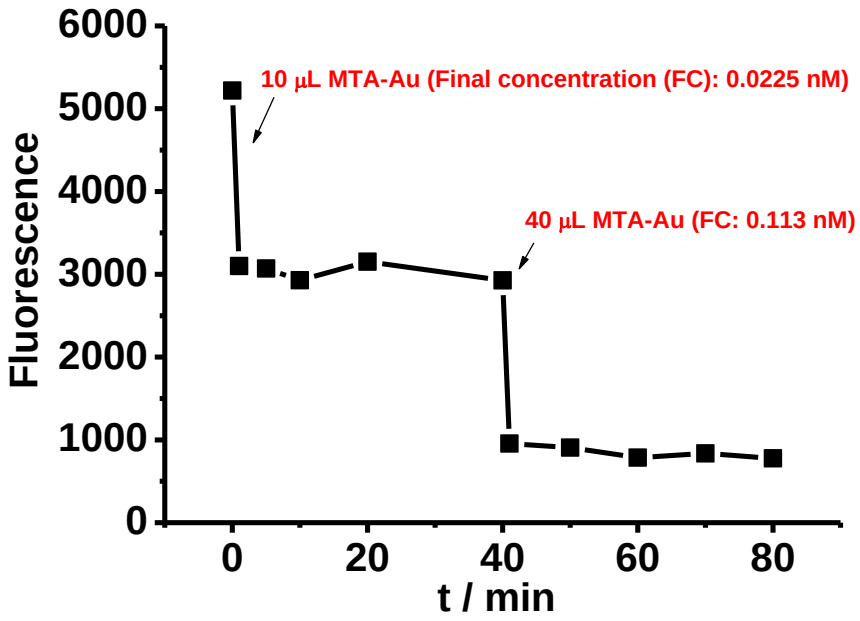

Figure S5. Time dependent quenching of the fluorescence of **4** (50 nM) in HEPES buffer (10mM, pH 7.0, 20% ethanol) upon the addition of MTA-Au.

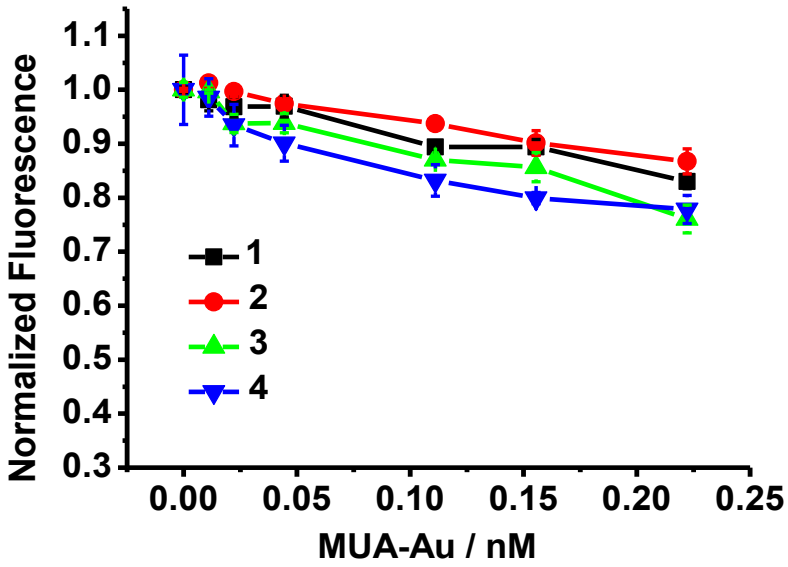

Figure S6. Fluorescence response of fluorescent probes (**1**-**4**, 50 nM) in the present of MUA-Au in HEPES buffer (10mM, pH 7.0, 20% ethanol); mean ± SD (n=3).

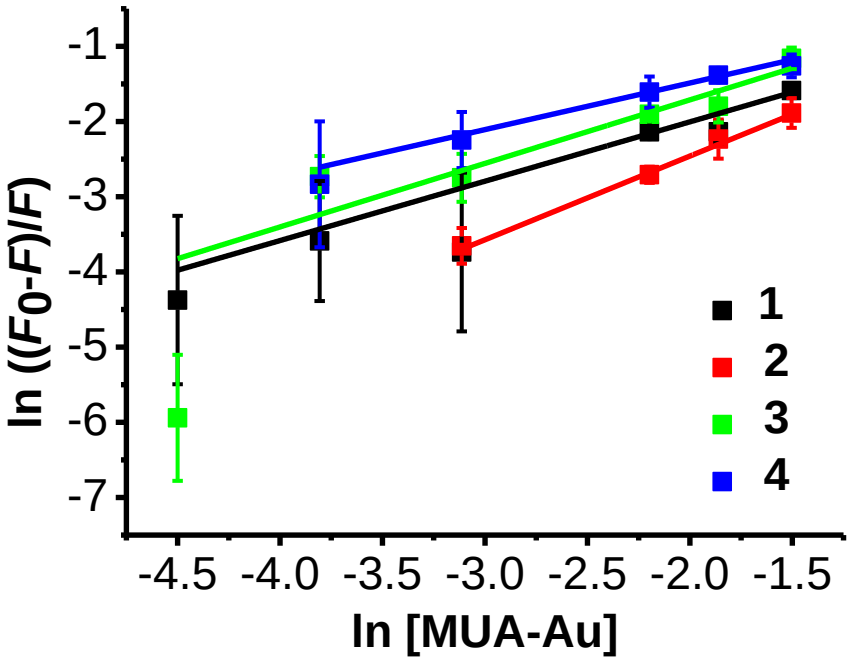

Figure S7. Fluorescence quenching data of **1**-**4** by MUA-Au fitted with Hill equation (solid line). The Hill coefficients obtained from the fluorescence quenching of **1**-**4** by MUA-Au are 0.79, 1.11, 0.84, and 0.62, respectively.

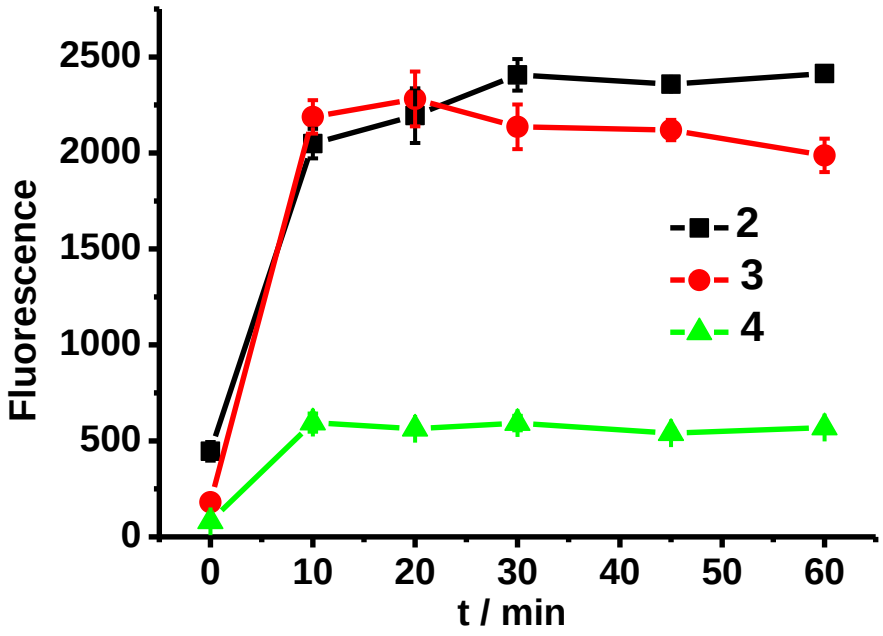

Figure S8. The kinetics of fluorescence turn-on of **2**-MTA-Au, **3**-MTA-Au, and **4**-MTA-Au system in the presence of LPS (50 nM) in HEPES buffer (10mM, pH 7.0, 20% ethanol); mean ± SD (n=3).

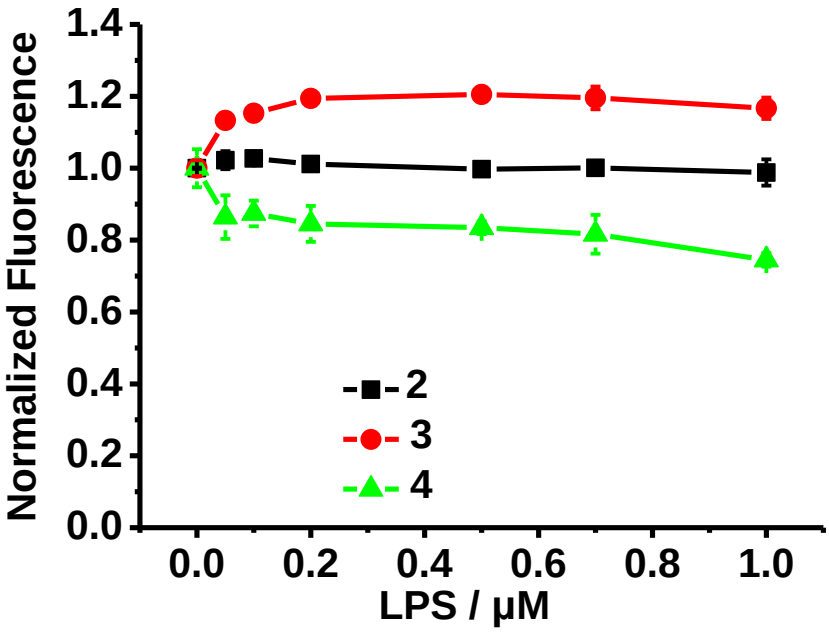

Figure S9. The effect of LPS on the fluorescence of **2**-**4** in HEPES buffer (10mM, pH 7.0, 20% ethanol); concentration of **2**-**4**: 50 nM; concentration of LPS ranging from 0 to 1 μM; data are presented as mean ± SD (n=3). It should be noted that the presence of LPS influences, to some extent, the fluorescence intensity of **2**-**4**, the effect which is, however, negligible as compared to the effect of Au NPs. Thus, the observed fluorescent recovery for the **2**/**3**/**4**-MTA-Au systems upon the addition of LPS was largely resulted from the dissociation of fluorescence probes from the surface of Au NRs.